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Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants

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Abstract

Sixteen data sets from four different pilot plant studies based on 30 wt% MEA solution as solvent have been simulated in four different commercial simulators and with two in-house codes. The simulations were performed on an as equal basis as possible given the constraints of the various simulators. Basically all the simulators are capable of giving reasonable predictions on overall performance, i.e. CO_2 absorption rate. The reboiler duties are less well predicted, as well as concentration and temperature profiles. For the reboiler temperature there is very much scatter.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

To combat the global temperature increase by capture and storage of CO_2 (CCS), optimization and improvement of the currently most viable capture option, absorption processes, will be decisive for widespread deployment of this technology. One of the most important tools for achieving this is high quality process simulators. One objective of the EU FP6 CAPRICE project is to collect operational data from four different pilot plants, validate these data,

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select a large set of runs based on data quality and their spread in conditions, and finally to validate a set of both commercial and in-house simulators against these data. The data sets are all for 30 wt% MEA operation and stem from the pilot plants at Esbjerg(CASTOR) , the University of Stuttgart(now at the University of Keiserslautern), the University of Regina, and SINTEF/NTNU. These pilots range in CO_2 capture capacity from about 10-1000 $kgCO_2/h$.
The simulators that were tested were the commercial codes: Aspen Rad Frac, Protreat, Promax, Aspen Rate Sep., and the in-house codes CHEMASIM from BASF SE and CO2SIM from SINTEF/NTNU.

2. Description of pilot plants and experimental program

The four different pilot plants are shown in figures 1 and 2.

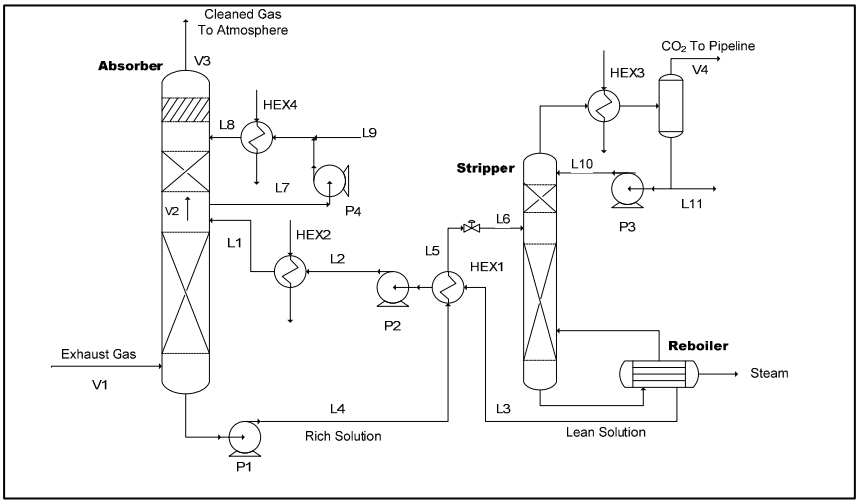


Figure 1 The Esbjerg CASTOR pilot plant, DONG Energy, the University of Kaiserslautern mini plant, and the ITC plant, University of Regina pilot

The Esbjerg CASTOR pilot plant

The flow sheet of the Esbjerg pilot plant is shown in Figure 1. The pilot plant operates on a slipstream of flue gas from the Esbjerg coal-fired power plant. The flue gas slip stream is taken downstream the wet FGD plant and does not undergo any pretreatment before supplied to the CO_2 absorption plant. The absorber consists of four consecutive packed beds with IMTP50 random packing. A water wash section is located on top of the absorber. A small stream (L9) of pure water is added to the wash section. The CO_2 concentration of the absorber inlet (V1) and outlet (V3) streams is continuously monitored by IR analyzers. The calibration of the analyzers is checked prior to each test and the analyzers are recalibrated if necessary. In addition, the flue gas flow to the absorber, the absorber temperature profile as well as the pressure drop are continuously measured. The stripper consists of two beds with IMTP50 random packing and a wash section on top. Condensate (L10) from the condenser is recycled to the wash section. The stripper pressure is controlled by an overhead regulation valve. The reboiler is driven by steam from the power plant. The flow of CO_2 from the condenser (V4) is continuously measured along with the stripper temperature and pressure at various positions. For all the tests conducted in CASTOR, the pilot plant was allowed at least three space times to reach steady state and each data point was an average of two hours steady state operation. During each test liquid samples of lean and rich MEA solution were collected at position L1 and L4, respectively. The liquid samples were analyzed for MEA and CO_2 by titration as outlined in (Ma'mun et al.[1]) and (Tobiesen et al.[2, 3]).

The ITC, University of Regina pilot plant

ITC pilot plant is operated to capture 1 tonne of CO_2 per day. Flue gas (V1) is generated by a natural gas boiler and micro turbine to supply a feed gas with CO_2 concentrations of 4% and 8% with a high oxygen concentration. A

booster fan is installed before the absorber to ensure a sufficient gas feed pressure into the absorber. The absorber is comprised of 3 sections packed with structured packing. On top of the top section is a wash water section to cool down the solution in order to minimize MEA loss. Each section is approximately 2.19 meter which includes packing support, packing material and liquid re-distribution. The packing material is Flexipac 700Y. Treated gas (V3) is released at the top of the absorber whereas the liquid solution flows downwards to the bottom of the absorber. A rich amine pump (P1) is integrated into a system to increase the liquid pressure to about 2 MPa before flowing through a rich-lean heat exchanger (HEX1) and then the desorber. The desorber is comprised of 3 sections packed with structured packing. The two bottom sections are approximately 3.22 meter while the top section is approximately 8.3 meter. The packing material is also Flexipak 700Y. At the top section of the desorber, it is integrated with a reflux process to separate the CO_2 product (V4) and the stream mainly containing water (L10) which flows back to the desorber. A reboiler is added at a bottom of the desorber to heat the liquid solution. The heat is supplied by a steam obtained from the natural gas boiler. The lean amine solution is cooled down to 40^{o}C by a cooler (HEX2) while a makeup unit is integrated before HEX2 to compensate for any MEA loss and to control the MEA solution concentration.

The concentration of flue gas and corrosion rate are respectively monitored by gas analyzers and corrosometer probes while temperature, pressure and mass flow rate are respectively measured by temperature probes, pressure gauges and mass flow rate meters. All instruments are connected to a controller (Delta V) which also collects and records data in real time. The CO_2 loading in the amine solution is measured by a titration technique. Liquid samples for this purpose are taken while the process is at steady state.

The University of Keiserslautern mini plant

For testing the process behavior of new solvents for CO_2 capture a pilot plant was constructed at the University of Kasierslautern. The basic flow sheet is identical with the one shown in Figure 1, pictures of the plant are shown in Figure 2. The flue gas is produced by a gas burner, SO_2 and other flue gas components can be added. The flue gas flow rate can be set between approximately 70 kg h^{-1} and 150 kg h^{-1}. The CO_2 partial pressure in the flue gas can be varied from 36 and 134 mbar by CO_2 recirculation A solvent flow rate between about 50 kg h^{-1} to 350 kg h^{-1} can be established. Absorber and desorber, including the washing sections, are equipped with the structured packing Mellapak 250.Y (Sulzer Chemtec, Winterthur, Switzerland). The diameter of the columns is 125 mm. The packing height in the absorber is 4.2 m, arranged in five sections. The desorber has a packing height of 2.5 m in three sections. Despite these dimensions, which exceed those of typical laboratory set-ups, we use the term mini plant here, as compared to equipment in power plants, the size of our plant is small. (Notz et. al. [4])

The measurement and control equipment of the mini plant allows taking all data which are necessary for the process analysis. For all important gas and liquid streams the volume / mass flow, temperature, pressure and composition are detected. At the absorber and desorber column temperature and concentration profiles of the liquid and the pressure drop are measured. The CO_2 content in the dry flue gas at the absorber inlet and the absorber outlet is detected by infrared absorption, the O_2 content with by Para magnetism. The overall concentrations of CO_2, water and amine in the liquid samples are detected with different techniques. The amine content is analyzed by Gas Chromatography, the water content by Karl-Fischer titration and the CO_2 content by titration with KOH.

In different parameter studies, like the variation of the solvent flow rate, stripper pressure, flue gas flow rate and CO_2 content in flue gas, the process behavior with a 30 wt-% MEA solution was investigated. For all four selected operation points of this plant the component mass balances and the heat losses were calculated.

The SINTEF/NTNU pilot rig

At the time of performing the reported pilot campaign, the SINTEF-NTNU rig looked as depicted in Figure 3. The rig was based on recycle of the gas flow and also of CO_2 and did not have a water wash section on the absorber. Both absorber and desorber used a Mellapak 250Y packing. The recycle gas could be cooled before return to the absorber. The CO_2 from the condenser is recycled back to the gas circulation fan inlet. Sampling of the gas phase was done right after the absorber exit, (V2), and just before the inlet, (V1), as shown in the figure. The outlet gas sampling is placed at a distance from the recycle CO_2 inlet such that the analysis should not be influenced by recycle CO_2. These CO_2 analyses were online using a calibrated IR instrument. Online temperature and pressure measurements were performed at the same positions. The liquid phase in and out of the absorber were sampled at positions before the final lean amine cooling, (L1), and at the absorber outlet, (L4). It was also sampled before

entering the storage tank, (L2). For the stripper the CO_2 from the condenser passed through a mass flow meter and its flow rate recorded on-line. The desorber did also not have an upper water wash section and the condensate from the overhead condenser was piped directly back to the desorber reboiler. The liquid phase, (L6) into the stripper was taken to have the same total composition as (L4). The desorber lean outlet, (L3), was taken to have the same composition as (L2). However, both pressure and temperature were recorded independently for these two flows. The liquid flow between stripper column and reboiler was sampled. All liquid samples were analyzed for amine and CO_2 content by titration, (see Tobiesen et al.[2,3], Ma'mun et al.[1]).

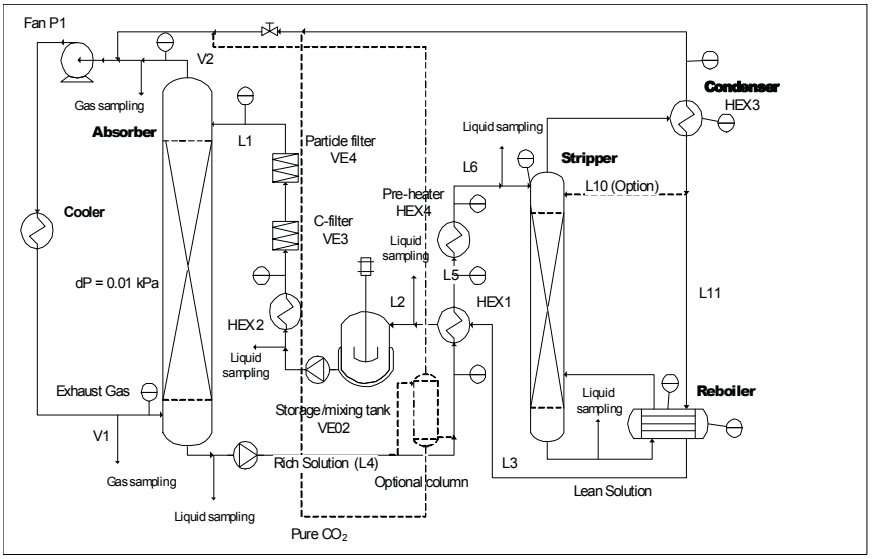


Figure 2 Pilot plant layout at SINTEF-NTNU

Table 1: Data for the 4 pilot plants

	Wash water section			Absorber			Stripper		
	Packing type	Diameter	Height	Packing type	Diameter	Height	Packing type	Diameter	Height
NTNU/SINTEF	N/A	N/A	N/A	Mellapak250Y	0.15m	4.36m	Mellapak250Y	0.1m	3.89m
DONG	Mellapak252Y	1.1m	3m	IMTP50	1.1m	17m	IMTP50	1.1m	10m
ITC, REGINA	Flexipac700Y	0.33m	2.93m	Flexipac700Y	0.33m	7.05m	Flexipac700Y	0.33m	9.97m
ITT, STUTTGART	Mellapak250Y	0,125	0.42m	Mellapak250Y	0.125m	4.2m	Mellapak250Y	0.125m	2.52m

3. Simulation software and common simulation basis

In the simulations we have tried as far as possible to adapt a common strategy. The whole flow-sheet was simulated for all cases and the basis was inlet gas and the lean amine entering the absorber, and as criterion for the desorber the lean amine outlet loading was set to the experimental one and the experimental total pressures were used.

Aspen Rad Frac: The four plant flowsheets were reproduced in Aspen Plus, v2006.5, using the equilibrium stage Radfrac modules to model absorber and stripper columns. With the focus on steady-state heat and mass balances around the columns tanks and pumps were neglected. Furthermore, disregarding the need for water and solvent make-up calculation, the lean solvent stream was teared and the balance of CO_2 and water (where positive) was externally converged by adapting the reboiler heat supply to match the lean loading entering the absorber as well as excess water removal from the stripper condensate reflux. A closed-loop simulation with water and solvent make-up stream calculation has initially been performed for one pilot experimental point (Dong, test 1) and confirmed equality of results to the faster converging teared flowsheet.

The methodology chosen to fit the absorber performance to the measured concentration and temperature profiles was to assume an abundant number of stages (25-35) and (a.) to adjust one constant stage efficiency for the CO_2 component in the entire column as well as (b.) the number of stages per packing section between the sampling

points. It was tried as an alternative to follow the recommendations given in the Aspen software documentation and keep the number of stages per packing section constant and calculate different absorption efficiencies in each section by specifying the measured gas concentrations along the column. This was not succesful for convergence reasons.

The stripper was modelled with a constant number of stages and stage efficiencies of unity, including a wash section where applicable. The condenser section was modelled as an external flash block at the given pressure and temperature. The reboiler heat duty was iterated to reproduce the given absorber input lean loading. The solvent-solvent heat exchanger was adapted to the hot outlet/ cold inlet temperature approach given by the pilot stream data.

Promax: ProMax is a commercial process modeling software developed by Bryan Research & Engineering. The software has the capability to design and optimize chemical processes and refineries. It is combined with Microsoft Visio® for users who are not or little familiar with computer aided design to enable the easy implementation of schematic diagrams. It is also embedded with more than 50 thermodynamic packages (i.e. Electrolytic-ELR and NRTL) with the integration of TSWEET used to simulate the amine sweetening processes.

It needs to be recognized that a conventional CO_2 capture process uses amines (e.g. MEA, DEA, MDEA and AMP) as the chemical absorbent to capture CO_2. In addition, the CO_2 capture process requires the involvement of chemical reaction, CO_2 kinetic and solubility models. ProMax is equipped with all the necessary models. Thus, its simulation result can be used to represent an actual CO_2 capture process. Therefore, this then allows the user to validate an existing CO_2 capture process and/or simulate a new conceptual design.

The simulation has been performed under the current operating conditions of ITC's pilot plant at the University of Regina. Constraint parameters have been included to regulate the simulations. These consist of:

1. Mass and energy balance with a low tolerance in a recycle loop.
2. Removal efficiency by an equation solver put on the solvent recirculation flow rate.
3. Stripper column reflux condenser temperature of 40^{o}C.
4. Temperature approach between rich amine solution inlet and lean amine solution outlet in HEX1 of 10^{o}C.

CHEMASIM: A process model of the CO_2 absorption in a MEA solution is implemented into the in-house simulation environment CHEMASIM. CHEMASIM is a powerful tool for steady-state simulations of chemical processes and was developed by BASF SE. CHEMASIM contains a non-equilibrium absorber / desorber model, including the rigorous calculation of heat and mass transfer between gas and liquid phase, taking into account the complete chemical reaction system, as well.

The two-film theory is used for the description of heat and mass transfer over the gas-liquid interface. The resulting partial differential equation system is solved numerically by discretization of column height and fluid films. With a non-equidistant arrangement of discrete elements in the liquid film, an accurate calculation of heat and mass transfer under the strong influence of the fast reaction between CO_2 and amine is enabled. (Asprion [5])

An Electrolyte-NRTL model is used for calculation of the component activity coefficients in the strongly non-ideal solution. The parameters were adapted to gas–liquid equilibrium measurements. The reaction data were taken from literature and fitted to own experimental results. When possible, standard mass transfer correlations with parameters from literature for the calculation of effective interfacial area and mass / heat transfer coefficients were used. The simulations of the pilot plant experiments at the ITC, University of Regina, were carried out with a fixed interfacial area because of missing parameters for the used structured packing.

All simulations were carried out completely predictive without any fitting to experimental pilot plant data. The flue gas inlet stream, the solvent flow rate and the rich-solvent temperature at the desorber inlet were defined in simulation as measured in the experimental study. The lean-loading at the absorber were fixed in the simulation to the experimental measured value to calculate the CO_2 removal rate and the reboiler energy.

Aspen Rate Sep.: An Aspen RateSep absorber model was created by IFP to simulate absorber pilot plant data from Campaign 2 of the CASTOR project. The pilot plant campaign 2 experiments were conducted using a 5M (30 wt%) monoethanolamine (MEA) solvent[6]. The model required the adjustment of : property data, the installation of high amine concentration, high CO2 loading kinetics, and the incorporation of hydrodynamic parameters.

The creation of the model required the modification of some property data within Aspen databanks. A heat of formation inconsistency was adjusted within the model. Heat capacity data was adjusted in the Aspen data banks to match VLE obtained heat of absorption data at temperatures other than 25C. The thermodynamic model used is

electrolyte NRTL. Also, parameters associated with density and viscosity were adjusted, especially for high MEA concentration and high loading.
Highly concentrated and highly loaded MEA rate data could match unloaded, dilute literature data when activity coefficient corrections were properly considered. This method is used to corrected the classical kinetic equation. The effect of ionic strength on the kinetics was quantified and implemented into the model.

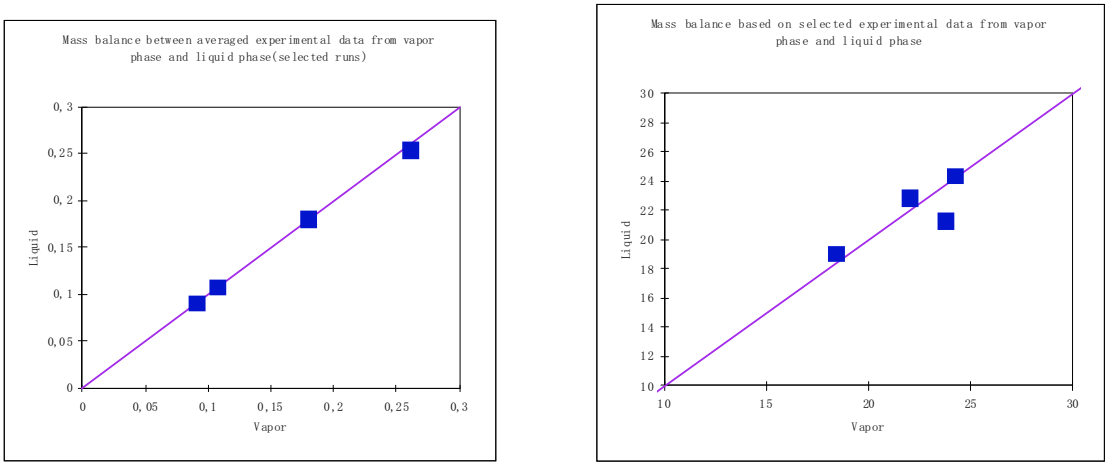
CASTOR specific hydrodynamic and mass transfer properties were also implemented into the model. Correlations developed by IFP were used to calculate the liquid holdup, interfacial area and the liquid film mass transfer coefficient. The interfacial area correlation for the model was developed from experimental tests performed at IFP and for IMTP 50 random packing which equipped the Castor pilot plant. The liquid holdup was also correlated from experimental tests performed at IFP. The gas film mass transfer coefficient was calculated via Onda and the liquid film mass transfer coefficient was input into the model as a constant. The Aspen RateSep absorber model does not use any fitting parameters to match results to the pilot plant[7].

ProTreat™: ProTreat™ is a commercial process rate based simulator specifically aimed at absorption processes made by Optimized Gas Treating Inc.. It uses a rate based approach to column modeling and several packing materials are included. All the packing materials used in these pilot studies could be simulated. It has two thermodynamic packages for the amine blends based on either a Kent-Eisenberg or a Lee-Mather approach. The Lee-Mather model was used for these simulations. The ProTreat model does not use any fitting parameters to match pilot plant results.

CO2SIM: CO2SIM is an in-house software package developed by NTNU and SINTEF. The simulator is restricted to absorption processes and has implemented a rate based approach. It is limited in number of packing materials and for this study the FlexiPack 700 had to be substituted with another packing with constant active interfacial area. For the IMTP 50 packing the correlations developed in CASTOR were used. As thermodynamic model a modified Deshmukh-Mather model was used for this study. The CO2SIM model does not use any fitting parameters to match pilot plant results [2,3].

4. Results

Validation of experimental data



a b

Figure 3. Examples of mass balance check on selected runs from the pilot plants, a) NTNU/SINTEF, b) DONG

The mass balance check on CO_2 was generally good in all runs, as illustrated by the results shown in Figure 3. This gave room for selection based on spread in rich and lean loading and in mass transfer rates.

Mass transfer rates

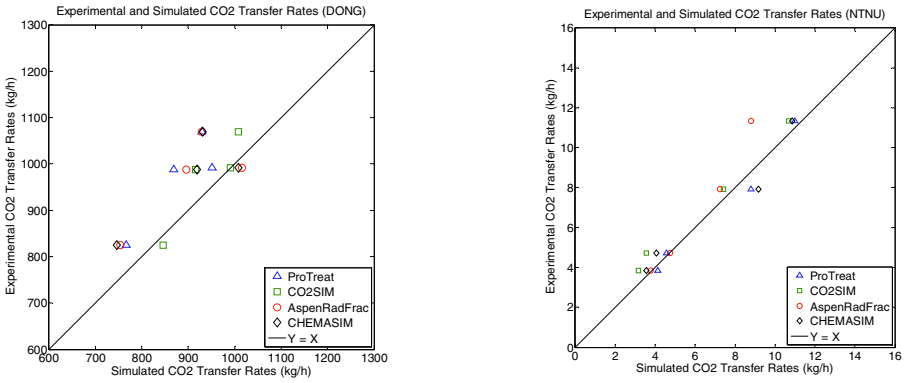


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Figure 4. Experimental and simulated mass transfer rates, a) DONG, b) NTNU/SINTEF

The mass transfer rates are predicted within about 5-10% accuracy. It can be seen that there is a tendency to under-predict the transfer rate at Esbjerg(DONG) whereas for the NTNU/SINTEF plant it is evenly distributed. The deviations are about the same in the two columns so no clear effect of column size is seen. It is interesting to note that Aspen Rad Frac, in spite of being a stage based model, does predict changes in operating conditions quite well.

Reboiler heat duty

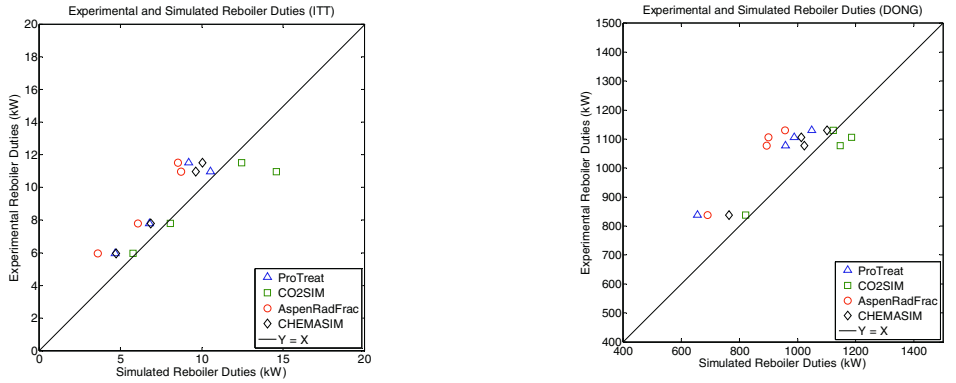

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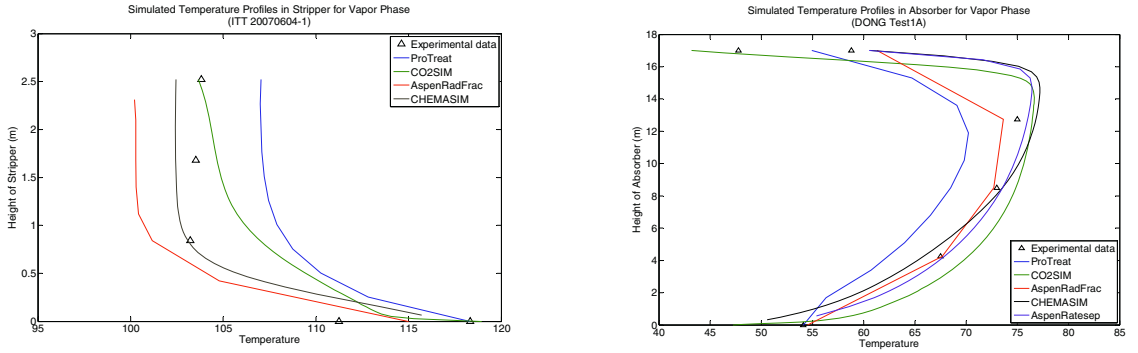
Figure 4. Examples of experimental and simulated reboiler duties, a) ITT Stuttgart, b) DONG

The basis for the simulated heat duties was the experimental lean loading. Generally more scatter is seen in the data than for mass transfer rates. This may not only be caused by less reliability in the simulations but also by higher uncertainty in the experimental data, e.g. caused by unaccounted for heat losses and uncertainties in the heat input.

Temperature profiles

Temperature profiles from the ITT Stuttgart stripper are shown in figure 5 a). This is a typical case and it can be seen that the simulators do not agree with each other and the departure from the experimental points is relatively large. The relative merits of the simulators varied from case to case and no one was better than the others. To predict temperature profiles in the desorber seem to be still very difficult. In figure 5b) profiles in the DONG absorber are used as an example. Here the agreement between the simulators is generally better and also the fit to experimental data. It should be noted that Aspen Rad Frac has been fitted to the actual experimental concentration profile in the case shown in figure 5b). This will also affect the temperature results of course. However it does show that if the mass transfer is well predicted then the temperatures follow.



a) b)

Figure 5 Temperature profiles in the stripper, ITT Stuttgart and in the absorber, DONG

Concentration profiles

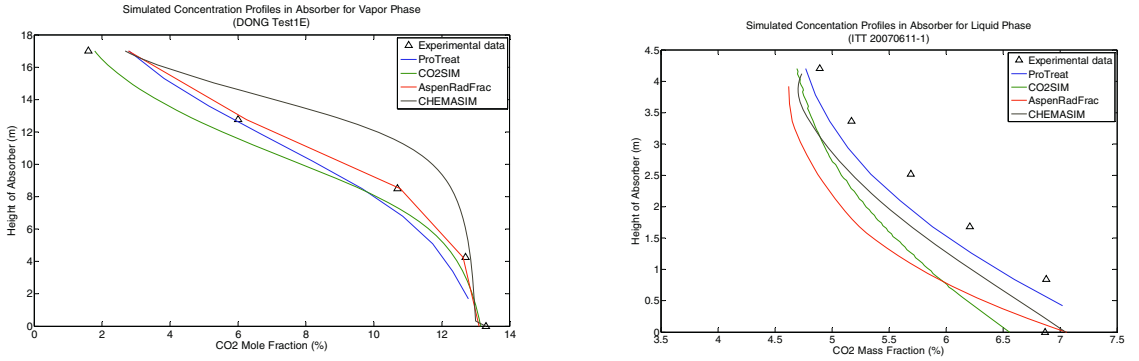


Figure 6 Gas and liquid phase concentration profiles from the DONG and ITT Stuttgart plants respectively. The absorber vapor phase profiles are in reasonable agreement with experimental data on the graph shown, but the variation from case to case was large. The liquid phase agreement is worse, and this was the trend for the liquid phase cureves from ITT Stuttgart. This may reflect the added difficulty represented by the liquid phase analyses.

References

[1] S. Ma'mun, V.Y. Dindore, and H.F. Svendsen, "Kinetics of the Reaction of Carbon Dioxide with Aqueous Solution of 2-((2-Amino(ethylamino)ethanol", Ind. Eng. Chem. Res., (2007), 46, 385-394

[2] F.A. Tobiesen, O.Juliussen, and H.F. Svendsen, "Experimental Validation of a Rigorous Absorber Model for CO_2 Postcombustion Capture", AIChE Journal (2007), 53(4),846-865

[3] F.A. Tobiesen, O.Juliussen, and H.F. Svendsen, "Experimental validation of a rigorous desorber model for CO_2 post-combustion capture.", Chem Eng. Sci., 63(10), 2008, pp 2641-2656

[4] R. Notz, N. Asprion, I. Clausen, H. Hasse: Selection and Pilot Plant Tests of New Absorbents for Post Combustion Carbon Dioxide Capture, Chem. Eng. Res. Des., 85 (2007) 510-515

[5] N.Asprion, "Non-equilibrium rate-based simulation of reactive systems: simulation model, heat transfer, and influence of film discretization", Ind. Eng. Chem. Res., 45 (2006) 2054 - 2069

[6] Dugas, R., P. Alix, et al. (2008). "Creation of an Aspen RateSep absorber model for the evaluation of castor pilot plant data." Preprint – American Chemical Society, Division of Petroleum Chemistry 53(1): 89-92.

[7] Ross Dugas, Pascal Alix, Eric Lemaire, Paul Broutin, Gary Rochelle, "Absorber Model for CO_2 Capture by Monoethanolamine -Application to CASTOR Pilot Results", GHGT9, Washington Nov 2008, Oral presentation and proceeding of the congress